

ELECTRONIC ABSORPTION SPECTRA OF 2-, 4-, 6- AND 7-METHYL QUINOLINE VAPOURS

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(Plate 4 and 5)

ABSTRACT. The near ultraviolet absorption spectra of four methyl-substituted quinolines, namely, 2-, 4-, 6- and 7-methyl quinolines, have been photographed for the first time in the vapour state. The spectra of these molecules occur approximately in the region $\lambda 3200 - \lambda 2800 \text{ \AA}$ and consist in each molecule of 10 to 15 rather broad, red-degraded bands. With the Raman and infra-red data on these molecules available in the literature, the spectra have been analysed. The most intense bands at the longest wavelength side are chosen as (0,0) bands and their wave numbers are $31999, 32152, 31759$ and 31836 cm^{-1} for 2-, 4-, 6- and 7-methyl quinolines respectively. No ground state frequencies have been recorded in these molecules despite the wide range of experimental conditions of study of the spectra, except for three weak fundamentals in 2-methyl quinoline. The fundamentals obtained in this work in each molecule account for most of the bands in the spectrum. The results obtained are reported and discussed.

INTRODUCTION

Although a good deal of work has been done on the ultraviolet absorption spectra in the vapour state of benzene and substituted benzenes, relatively not much work has been done on two-ring molecules and, in particular, on heteroatomic two-ring compounds. Therefore it was thought worth while to investigate in the vapour state the electronic absorption spectra of some of these heteroatomic molecules with two fused six-membered rings. As a first step in that direction, the near ultraviolet absorption spectra of four methyl-substituted quinolines, namely, 2-, 4-, 6- and 7-methyl quinolines have been investigated in the vapour state for the first time. The ultraviolet absorption spectra of these methyl quinolines have been studied in solution before (Knight *et al.* 1955; Pickard *et al.* 1947) and λ_{max} (wavelength of maximum absorption) and ϵ (extinction coefficient) reported. The infra-red spectra of all these molecules have been investigated by Shindo and Ikeawa, (1956), Shindo, (1960) and Katritzky and Alan Jones (1960), while the Raman spectra of only 2- and 4-methyl quinolines have been reported in the literature Luther and Reichol, 1950; Jatkari Kulkarni 1936). A preliminary note reporting the results of our investigation of the ultraviolet spectra in the vapour state of these four molecules has been published (Shashidhar *et al.* 1966). In this paper are reported the details of the investigation.

EXPERIMENTAL

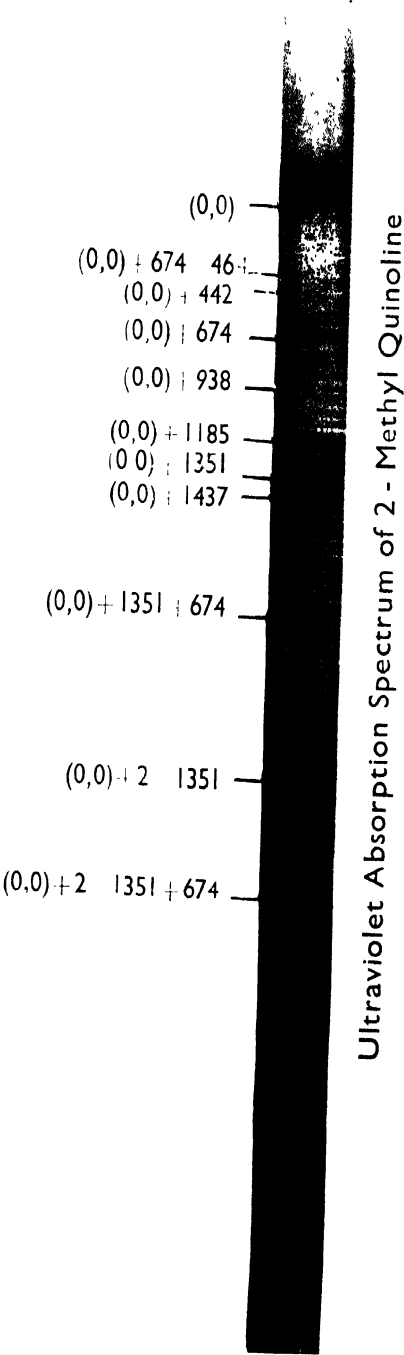
The samples of 2-, 4-, 6- and 7-methyl quinolines used in this investigation were supplied by Light and Co, England and were stated to be very pure. The boiling points of 2-, 4-, 6- and 7-methyl quinolines were 246°C, 258°C, 252°C, 248°C respectively. They were further purified by distillation in vacuum and the distilled products were used for work. Using absorption cells of lengths 5, 10, 25, 50, 75, 100, 150, 175 and 200 cm (the cells of the first three lengths were of quartz and the longer ones were of pyrex with pyrex to quartz graded seals), varying the temperature from that of the room to 200°C and eliminating the possibility at higher temperatures of the vapour condensing on the windows by keeping the main body of the absorption cell at about 10°C higher in temperature than the liquid container, spectra were photographed under conditions of saturated vapour pressure on a Hilger medium quartz spectrograph using Ilford R-40 and G-30 plates. A Hilger deuterium-filled lamp run on a stabilized power supply served as the source of continuum. The exposure time varied from about half an hour to a few hours. The bands were measured on five different spectrograms with reference to iron standards and the wavelengths computed with Hartmann's dispersion formula. The mean value of the different determinations was taken for the wavelength of each band. Because the bands are rather broad, the accuracy is estimated to be in general about 10 cm⁻¹.

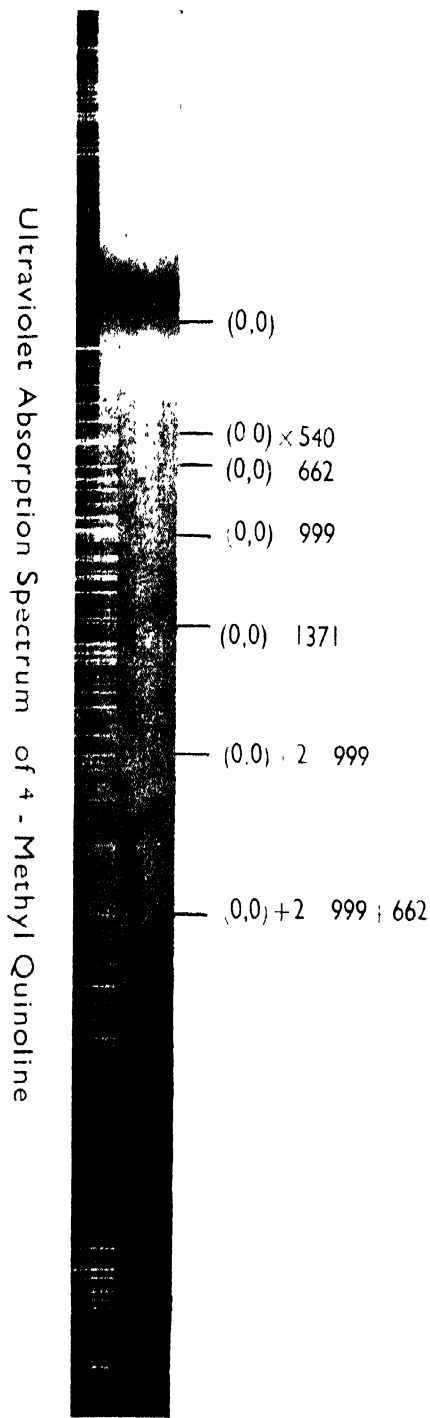
RESULTS AND ANALYSIS

The electronic absorption bands of the methyl quinolines studied occur approximately in the region λ 2800 to λ 3200 Å. The bands are rather broad and degraded to the red. In all these molecules the minimum number of bands was obtained at room temperature with a path length of 25 cm. The most intense band at the longest wavelength in each molecule has been taken as the (0,0) band. With the (0,0) band chosen in this way the bands of each molecule have been analysed with the help of the existing Raman and infra-red data. The wave numbers of the bands in vacuum, the visual estimates of their relative intensities, their separations in cm⁻¹ from the (0,0) band and their assignments are given in tables I, II, III and IV for 2-, 4-, 6- and 7-methyl quinolines respectively. Plates (4A, 4B, 5A and 5B) give enlarged reproductions of the spectra of the molecules investigated.

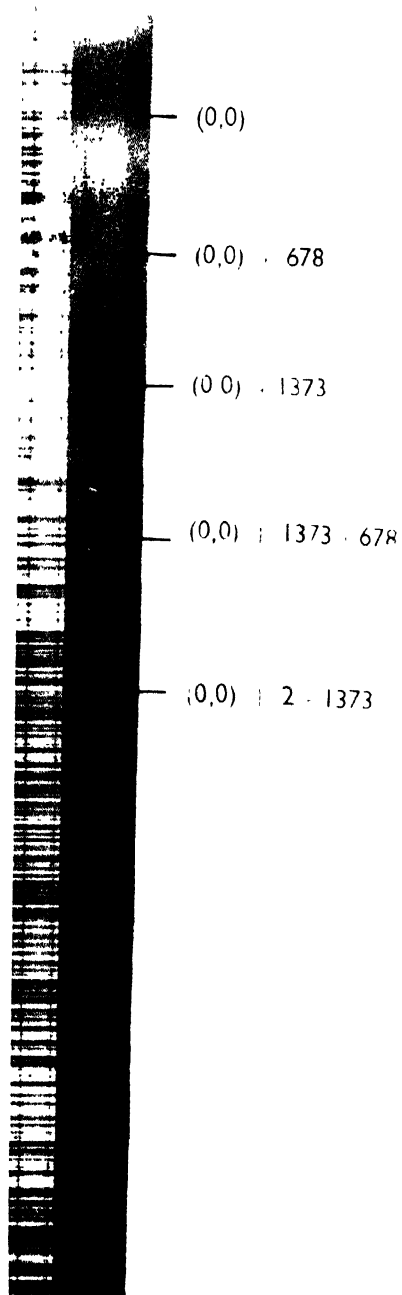
DISCUSSION

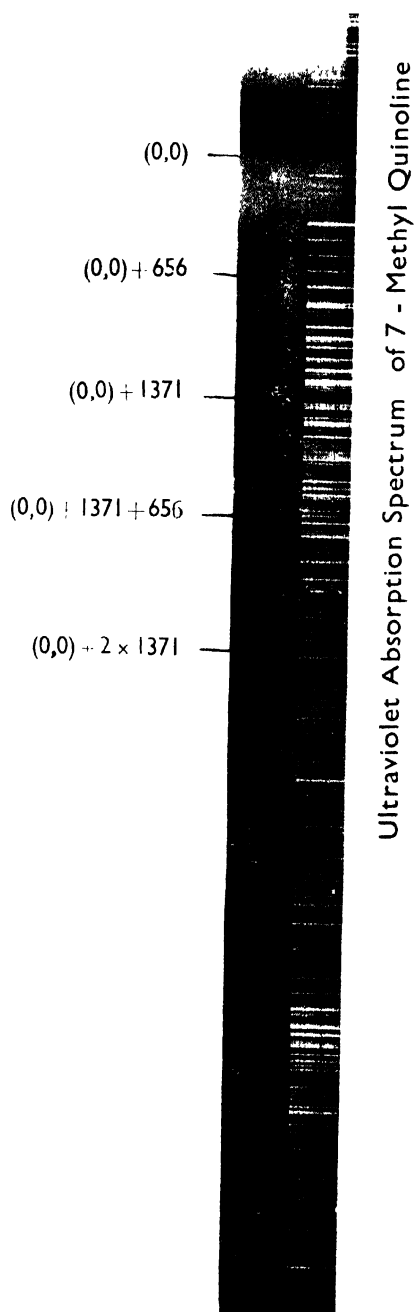
Each of the molecules studied in this work has a plane of symmetry which is the plane of the molecule, assuming the methyl group to be a single unit and therefore, they all belong to the point group, C_s . The observed band system in each of these molecules which corresponds to the forbidden transition in benzene, ${}^1A_{1g} \rightarrow {}^1B_{2u}({}^1L_b \rightarrow {}^1A)$ is ascribed to ${}^1A' \rightarrow {}^1A'$, which becomes allowed because of reduction in symmetry. It seems probable that in these molecules just as in the





Ultraviolet Absorption Spectrum of 6-Methyl Quinoline





case of quinoline vapour, there may also occur an $n-\pi^*$ system almost in the same region. We think, however, that the bands of the $n-\pi^*$ transition may be masked by the stronger, observed $\pi-\pi^*$ bands and that they are likely to contribute more to the background absorption in this region.

Ultra-violet absorption spectra of Methyl Quinolines in the vapour state

TABLE I
2-methyl Quinoline

| Wave number in cm^{-1} | Intensity | Separation in cm^{-1} from (0,0) band | Assignment |
|---------------------------------|-----------|---|----------------|
| 31280 | 0 | -719* | 0,0-719 |
| 31473 | 0 | -526 | 0,0-526 |
| 31535 | 0 | -464 | 0,0-464 |
| 31659 | 0 | -340 | 0,0-719+442 |
| 31999 | 6 | 0 | 0,0 |
| 32212 | 0 | 213 | 0,0+614-464 |
| 32441 | 1 | 442 | 0,0+442 |
| 32673 | 2 | 674 | 0,0+674 |
| 32937 | 1 | 938 | 0,0+938 |
| 33184 | 0 | 1185 | 0,0+1185 |
| 33350 | 2 | 1351 | 0,0+1351 |
| 33436 | 3 | 1437 | 0,0+1437 |
| 34035 | 1 | 2036 | 0,0+1351+674 |
| 34718 | 1 | 2719 | 0,0+2×1351 |
| 35390 | 0 | 3391 | 0,0+2×1351+674 |

*The error in measurement of this band is believed to be more because of its diffuseness and low intensity.

In all these molecules, there are two strong upper state frequencies which are progression-forming and also occur in combinations, the higher frequency being more intense. Each of them has about the same value in all the four molecules and they are : 674, 1351; 662, 1371; 678, 1373 and 656, 1371 in 2-, 4-, 6- and 7-methyl quinolines respectively. The more intense one around 1370 cm^{-1} may be a totally symmetric C-C stretching vibration (Gama C stretching) corresponding to the strong Raman frequencies 1376 cm^{-1} in naphthalene and 1372 cm^{-1} in quinoline. The other one around 670 cm^{-1} may be a totally symmetric vibration corresponding to the strong in-plane skeletal-distortion Raman frequencies 760

TABLE II
4-methyl Quinoline

| Wave number in cm^{-1} | Intensity | Separation in cm^{-1} from (0,0) band | Assignment |
|---------------------------------|-----------|---|---------------|
| 31871 | 0 | -281 | |
| 32032 | 0 | -120 | |
| 32152 | 6 | 0 | 0,0 |
| 32692 | 1 | 540 | 0,0+540 |
| 32814 | 0 | 662 | 0,0+662 |
| 33150 | 1 | 999 | 0,0+999 |
| 33347 | 0 | 1195 | 0,0+1195 |
| 33523 | 2 | 1371 | 0,0+1371 |
| 34144 | 1 | 1992 | 0,0+2×999 |
| 34804 | 0 | 2652 | 0,0+2×999+662 |

TABLE III
6-methyl quinoline

| Wave number in cm^{-1} | Intensity | Separation in cm^{-1} from (0,0) band | Assignment |
|---------------------------------|-----------|---|--------------|
| 31415 | 0 | -344 | |
| 31575 | 0 | -184 | |
| 31759 | 6 | 0 | 0,0 |
| 32031 | 0 | 272 | |
| 32265 | 0 | 506 | 0,0+506 |
| 32437 | 1 | 678 | 0,0+678 |
| 32624 | 0 | 865 | 0,0+865 |
| 32826 | 0 | 1067 | 0,0+1067 |
| 33132 | 2 | 1373 | 0,0+1373 |
| 33636 | 0 | 1877 | 0,0+1373+506 |
| 33839 | 0 | 2080 | 0,0+1373+678 |
| 34498 | 0 | 2739 | 0,0+2×1373 |

TABLE IV
7-methyl Quinoline

| Wave number in cm^{-1} | Intensity | Separation in cm^{-1} from (0,0) band | Assignment |
|---------------------------------|-----------|---|----------------------|
| 31503 | 0 | —333 | |
| 31639 | 0 | —197 | |
| 31836 | 6 | 0 | 0,0 |
| 31931 | 0 | 95 | |
| 32237 | 0 | 401 | 0,0 + 401 |
| 32492 | 1 | 656 | 0,0 + 656 |
| 32932 | 0 | 1096 | 0,0 + 1096 |
| 33207 | 2 | 1371 | 0,0 + 1371 |
| 33583 | 0 | 1747 | 0,0 + 1096 + 656 |
| 33854 | 0 | 2018 | 0,0 + 1371 + 656 |
| 34571 | 0 | 2735 | 0,0 + 2 × 1371 |
| 35208 | 0 | 3372 | 0,0 + 2 × 1371 + 656 |

TABLE V

| Molecule | Ground state frequencies in cm^{-1} | | | upper state frequencies (Present work) in cm^{-1} |
|--------------------|---|---------|-----------|--|
| | ultra-violet absorption (Present work) | Raman | Infra-red | |
| 2-methyl quinoline | 464(0) | 455(4) | — | 442(1) |
| | 526(0) | 522(5) | — | — |
| | 719(0) | 769(6) | — | 674(2) |
| | — | 1011(3) | 1015 | 938(1) |
| | — | 1270(1) | 1254 | 1185(0) |
| | — | 1372(7) | 1380 | 1351(3) |
| | — | 1465(2) | 1473 | 1437(3) |
| 4-methyl quinoline | — | 565(7) | — | 540(1) |
| | — | 705(8) | — | 662(0) |
| | — | 1068(6) | — | 999(1) |
| | — | — | 1294 | 1195(0) |
| | — | 1361(8) | 1361 | 1371(2) |
| 6-methyl quinoline | — | — | — | 506(0) |
| | — | — | — | 678(1) |
| | — | — | — | 865(0) |
| | — | — | 1145 | 1067(0) |
| | — | — | 1376 | 1373(2) |
| 7-methyl quinoline | — | — | — | 401(0) |
| | — | — | — | 656(1) |
| | — | — | 1139 | 1096(0) |
| | — | — | 1385 | 1371(2) |

and 758 cm^{-1} in naphthalene and quinoline respectively. In the 2- and 4-methyl quinolines, the corresponding Raman frequencies are 769(6), 1372(7) and 705(8), 1361(8) respectively. While the lower frequency has decreased in the upper states of these molecules, the higher one seems to remain almost unchanged.

It has not been possible to assign two to three bands in three of these spectra because, despite the fact that the spectra have been taken under all possible experimental conditions, no ground state fundamentals have been obtained for these molecules.

The correlations between the frequencies obtained in this work and the Raman and the infra-red data where available are shown in Table V, in which are also given for comparison, the corresponding data of naphthalene, [*U, V*—absorption data : (Sporer and Cooper, 1955); Raman and Infra-red data : (Lippincott and O' Reilly, 1955)].

The infra-red data of these molecules in the literature are not available to us. The infra-red data given in the Table are solution data taken from Katritzky and Alan Jones. They are not actually of methyl quinolines but are values obtained by the authors from their infra-red solution measurements on many substituted quinolines including the different methyl quinolines. They are, however, believed to be useful enough for correlation purposes since the authors state that the positions of these bands are relatively constant for different substituents while their intensities vary with the substituent. Therefore their intensities are not given in the table

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